Nanomaterials

2nd year Medical Physics

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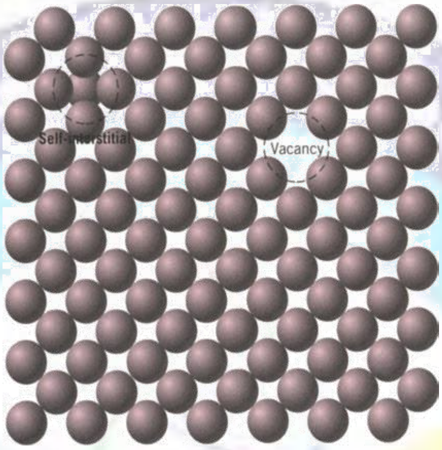
Lecture 4: Crystalline Irregularities



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4.1 Magnetic properties

The magnetic induction (B) represents the magnitude of the internal field strength within a substance that is subjected to a magnetic field (H). The units for B are teslas [or webers per square meter (Wb/m2)].

The relationship between B & H is represented by:

$$\mu = \frac{B}{H}$$

Where μ is called the permeability, which is a measure of permeable the material to applied magnetic field. It has units of webers per ampere-meter (Wb/A-m).

However, when a magnetic field is applied (H) on a material, the generated magnetic induction (B) in the material is a result of the external field strength (H) and the net magnetic moment of the material (M). This magnetic induction is expressed by:

$$B = \mu_0 (H + M)$$

where μ_0 is the permeability of free space ($4\pi\times10^{-7}$ Wb/A.m) and M is the magnetisation of the material. Each material will have a different M because of the differences in the number of electrons in atoms and molecules.

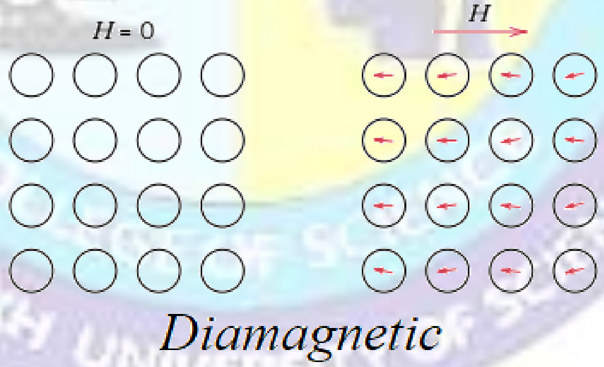
The relationship between the applied field and the magnetisation of the sample is known as the magnetic susceptibility (χ), which is expressed by:

$$\chi = \frac{M}{H}$$

The magnetic susceptibility values are characteristic to each particular material.

Materials may be categorised according to their susceptibility to the magnetic field applied. These categories are:

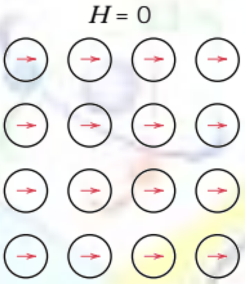
1. **Diamagnetic** materials, which have small and negative values of $\chi<1$, such as: Cu, Au and Si. Diamagnetic materials have no magnetic moment in the absence of applied magnetic field and their magnetisation is very low compared to other types of magnetism even with high applied magnetic field.



2. **Paramagnetic** materials where χ is typically small and positive ($<10^{-3}$), such as: Al and Na. Paramagnetic materials have a random magnetic moment in the absence of applied magnetic field and their magnetisation is low with small applied magnetic field.

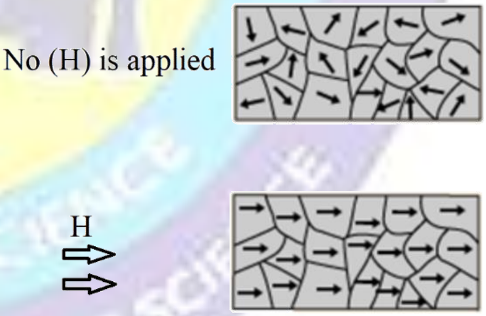
Paramagnetic

3. **Ferromagnetic** materials where χ is positive and larger compared to previous categories (>10^3). Ferromagnetic materials have a magnetic moment in the absence of applied magnetic field and their magnetisation is very high compared to other types of magnetism even with small applied magnetic field. Examples of ferromagnetic elements are Ni, Co, Fe and Gd. Ferromagnetic materials are very useful and the ferromagnetic behaviour is the base for a wide range of everyday applications.



Ferromagnetic

At normal temperatures, the magnetic structure of **ferromagnetic materials consists of regions** of uniform magnetisation known as the magnetic domains. The magnetisation alignment is the same inside each domain, but has different alignment to other domains. These domains are created in order to decrease the system energy. The net magnetisation of the material after domains are created is zero.



4.2 Crystal irregularities

We have studied the idea of crystal structures and we assumed that perfect order exists throughout the material on an atomic scale.

However, such an idealized solid does not exist; all contain large numbers of various defects or imperfections.

As a matter of fact, many of the properties of materials are sensitive to these crystalline imperfections. The influence is not always adverse, and often the introduction of controlled amounts or numbers of particular defects is intentional.

We’ll focus here on crystalline defects and surface effect:

4.2.1 Defects

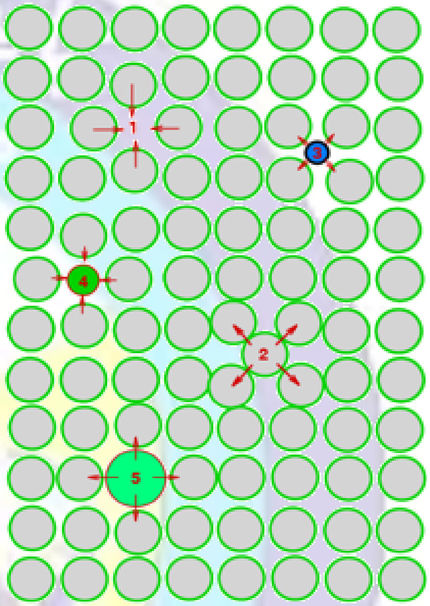
A **crystalline defect** is meant a lattice irregularity having one or more of its dimensions on the order of an atomic diameter.

Defects have a profound impact on the various properties of materials, for example: The process of forging depends on introducing defects to iron to improve its mechanical properties. In addition, point defects are important in semiconducting materials.

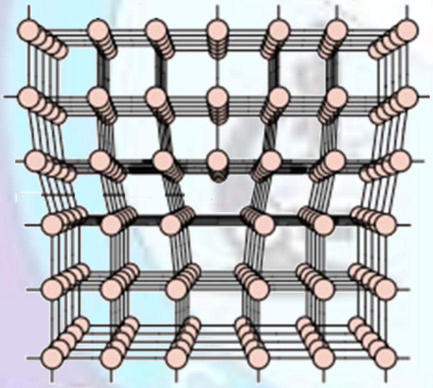
Defects are responsible for colour (& price) of a diamond crystal.

Defects may be classified into four categories depending on their dimension:

1. 0D, Point defects: atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).
2. 1D, Linear defects: groups of atoms in irregular positions (e.g. screw and edge dislocations)
3. 2D, Planar defects: the interfaces between homogeneous regions of the material (e.g. grain boundaries, external surfaces)
4. 3D, Volume defects: extended defects (pores, cracks)



1. Vacancy.
2. Self-interstitial
3. Impurity
4. Substitutional (smaller)
5. Substitutional (bigger)



Dislocation

4.2.2 External surface

The periodicity of atomic structures is disrupted at the surface of the material where be at the edge of that material. This also occurs at interfaces that separate phases inside the material.

For this reason, the number of nearest-neighbour atoms of an atom that is located at a surface is reduced.

Hence, the crystal structure of the material will be distorted at the surface.

This will give rise to differences in bonding and electronic structure and leading to the well-known phenomenon of surface tension or surface energy.

In bulk solid materials, the ratio of surface area to the material volume is very low. For this reason, the number of atoms at the surface is extremely low compared to the total number of atoms of the material.

4.3 Effects of nanometre length scale

In Bulk solid materials, electrons are free move inside the volume (**remember** electron cloud). Decreasing the material size will narrow that volume and electrons tend to be more localised in nanomaterials compared to bulk materials.

The electronic properties of a solid become severely distorted and the electrons in a reduced-dimensional system tend to behave more like the 'particle in a box' description.

This will lead to changes in the associated atomic structure. Such effects are generally termed quantum confinement.

Quantum confinement: the localisation of electrons movement inside the solid material due to the reduction of its size down to the nanometre scale.

Thus if the number of atoms in a system, hence the length scale, is substantially different to that in a normal bulk material, the energies and energy separations of the individual electronic states will be very different.

4.3.1 Change to the system total energy

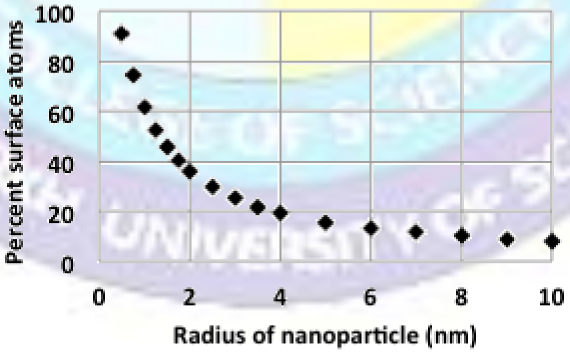
The main effect of these alterations to the bulk electronic structure is to change the total energy and hence the thermodynamic **stability** of the reduced length scale system relative to that of a normal bulk crystal.

This can have a number of important implications. It may change the most energetically stable form of a particular material; for example, small nanoparticles or nanodimensional layers may adopt a different crystal structure from that of the normal bulk material.

4.3.1 Changes to the system structure

In a small isolated nanoparticle, a large proportion of the total number of atoms will be present either at or near the free surface.

For instance, in a 5 nm particle approximately 30–50% of the atoms are influenced by the surface, compared with approximately a few percent for a 100 nm particle.



Such structural differences in reduced-dimensional systems would be expected to lead to very different properties from the bulk.

For example, some metals which normally adopt a hexagonal close-packed (*hcp*) atomic arrangement have been reported to adopt a face-centred cubic structure (*fcc*) in confined systems.

These changes are very likely to lead changes in the nanomaterial properties compared to their bulk size samples.

Nanocrystals are predicted to be essentially **vacancy-free**.

The small size of nanomaterials prevents any significant vacancy concentration.

This has important consequences for all thermomechanical properties and processes, which are based on the presence and movement of vacancies in the lattice.

Finally, **dislocations would have a less role to play on the properties of nanocrystals** compared to microcrystals. This is because of the dominance of crystal surfaces and interfaces.

4.4 Effect of nanoscale on properties

4.4.1 Structural properties

The increase in surface area and surface free energy with decreasing particle size leads to changes in interatomic spacing.

Metallic nanoparticles, such as gold, are known to adopt polyhedral shapes such as cube–octahedra. Some nanoparticles take decahedron and icosahedron shapes.

These arrangements are not crystals but are known as **quasiperiodic crystals**, which have no long-range periodic order similar to cubic crystals.

4.4.2 Chemical properties

Reduction of system size to nanoscale may change the chemical reactivity.

Nanoscale structures such as nanoparticles and nanolayers have very high surface area to volume ratios and different crystalline structures, which may lead to a radical alteration in chemical reactivity.

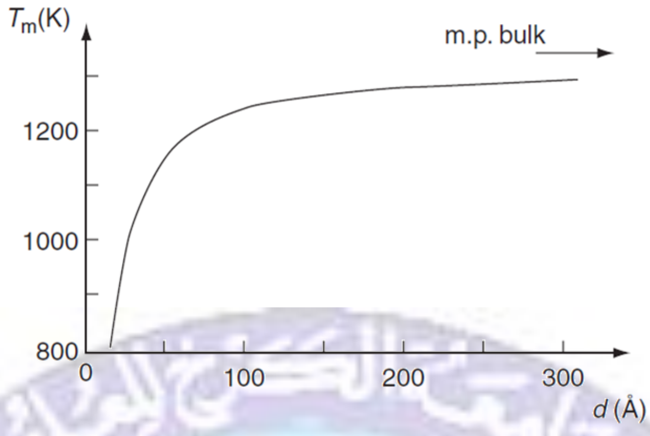
For example, many new medicines are insoluble in water at micron-size but will dissolve easily when in a nanostructured form.

4.4.3 Thermal properties

The large increase in surface energy and the change in interatomic spacing affects the thermal properties.

For instance, the melting point of gold particles has been observed to decrease rapidly for particle sizes less than 10 nm.

On other hand, matrices of metallic nanocrystals have higher melting points.



The variation in melting point of gold nanoparticles as a function of particle size

4.4.4 Mechanical properties

Many mechanical properties, such as toughness, are highly dependent on the presence of defects within a material.

As the system size decreases, the ability to support such defects becomes increasingly more difficult and mechanical properties will be altered accordingly.

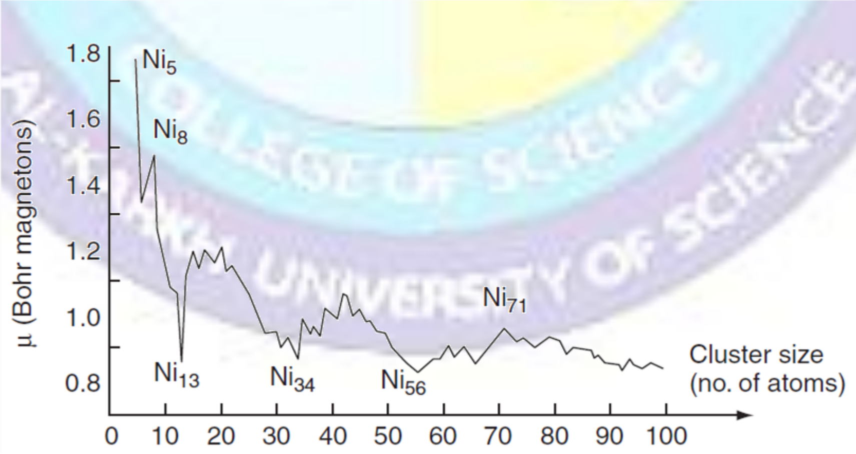
Novel nanostructures will show very different mechanical properties.

For example, carbon nanotubes show high mechanical strengths and high elastic limits.

Many nanostructured metals and ceramics are observed to be superplastic

4.4.5 Magnetic properties

The large surface area to volume ratio lead to different magnetic properties in nanomaterials compared to bulk materials. The figure below shows the magnetic moments of nickel nanoparticles as a function of cluster size.



Small magnetic nanoparticles often consist of only one domain and exhibit a phenomenon known as **Superparamagnetism**.